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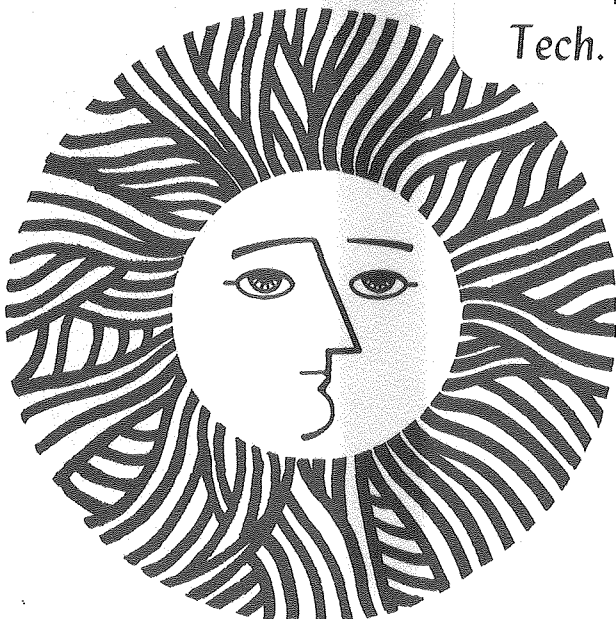## UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT
DIVISION

APPLICATION OF THERMAL ANALYSIS AND PHOTOELECTRON
SPECTROSCOPY FOR THE CHARACTERIZATION OF
PARTICULATE MATTER

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APPLICATION OF THERMAL ANALYSIS AND PHOTOELECTRON SPECTROSCOPY
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ABSTRACT

Photoelectron spectroscopy (ESCA) and thermal evol-
ved gas analysis (EGA) have been applied to charac-
terize sulfur- and nitrogen-containing species in
atmospheric particulate matter. Particulate amines
and amides previously identified only by ESCA have
been detected by EGA, a bulk method, for the first
time. EGA and ESCA results suggest the existence
of a sulfate similar to ammonium sulfate but with
some of the ammonium ions replaced by a charged
organic nitrogen complex.

Carbon-, nitrogen-, and sulfur-containing species account for
most of the mass of aerosol particles. In spite of years of
effort by many investigators, the exact chemical forms of carbon,
sulfur, and nitrogen in these particles are not known; nor are the
formation mechanisms of these species known with certainty. There
are many reasons for this situation, including the complexity of
the system and the dependence of the apparent chemical composition
on the analytical methods used. For example, wet chemical anal-
yses of sulfur and nitrogen species report only ions in solution.
These ions, however, may be originally water soluble (e.g.,
nitrate and ammonium from ammonium sulfate), or they may be ionic
products of hydrolyzable species such as amides (1). Of course,
insoluble species will not be detected by wet chemical techniques.

In contrast, methods such as photoelectron spectroscopy
(ESCA) analyze the entire sample content without sample prepara-
tion. However, ESCA is a surface technique, and the sample is
exposed to vacuum and X-ray bombardment during analysis. ESCA
results therefore may not be representative of the bulk composi-
tion; some volatile species may be lost because of the vacuum,
and in principle the X-ray bombardment may cause chemical changes
of some species.

Because of these possible problems, it seemed desirable to
employ a technique that will analyze the bulk properties of

particles without chemical treatment or preseparation of the sample and to compare these results with ESCA results. Thermal analysis in the evolved gas analysis (EGA) mode is one such technique. We will present some results of the application of ESCA and EGA to the characterization of sulfur and nitrogen species in atmospheric particulate matter.

Methods and Procedures

The ESCA method (2) and its application to aerosol particles (3) have been extensively discussed in the literature and will not be described here. In EGA the sample is heated at a predetermined rate in an oxidizing or neutral atmosphere. The evolved gases resulting from volatilization, decomposition, and combustion of the sample are monitored as a function of temperature by one or more gas-specific detectors. The carrier gas is usually oxygen or nitrogen. For analysis of carbonaceous materials, the gas detected in the oxygen mode is CO_2. For analysis of nitrogeneous species, we use oxygen as the carrier gas and detect total nitrogen oxides, NO_x.

A schematic representation of the EGA apparatus used in our analysis of aerosol particles is shown in Figure 1. The sample, collected on a prefired quartz filter, is placed in the quartz combustion tube so that its surface is perpendicular to the tube axis. The tube is supplied with purified oxygen, with excess oxygen escaping through an axial opening at the end of the tube.

The remainder of the oxygen (together with gases produced during analysis) is pulled at a constant rate determined by a critical orifice through a nondispersive infrared CO_2 analyzer (MSA LIRA 202S) and then through a chemiluminescent NO_x analyzer (Thermo-Electron Model 14D). Material may be evolved from the sample by volatilization, pyrolysis, oxidation, or decomposition. To ensure complete conversion of all carbon to CO_2, a section of the quartz tube immediately outside the programmed furnace is filled with a CuO catalyst bed which is kept at a constant 900°C by a second furnace. This is especially necessary at relatively low temperatures (< 250°C) where volatilization and incomplete combustion are the dominant processes occurring in the carbonaceous component.

Analyte gas concentrations are monitored as a function of temperature, and the resultant "thermogram" is a plot of concentration vs. temperature with the integrated area of the curves being proportional to the carbon or nitrogen content of the sample. Quantitation is effected by calibration with gases of known concentration and by measuring the gas flow rate through the system. This calibration is verified by analyzing samples of quantitatively known elemental content.

The thermograms of ambient and source aerosol samples reveal distinct features in the form of peaks or groups of peaks. One important component of the carbonaceous aerosol is graphitic

carbon, which is known to cause the black or grey coloration of ambient and source particulate samples (4). To determine which of the thermogram peaks corresponds to this graphitic carbon, we monitor the intensity of a He–Ne laser beam which passes through the filter. This provides simultaneous measurement of sample absorptivity and CO_2 evolution. The light penetrating the filter is collected by a quartz light guide and filtered by a narrow band interference filter to minimize the effect of the glow of the furnaces. An examination of the CO_2 and light intensity traces enables the assignment of the peak or peaks in the thermograms corresponding to the black carbon because they appear concurrently with the decrease in sample absorptivity.

The potential of this method (in the CO_2 mode)(5) is illustrated in Figure 2, where the complete thermogram of an ambient sample is shown. The lower trace represents the CO_2 concentration, while the upper curve corresponds to the light intensity of the laser light beam that reaches the detector during the temperature scan. Inspection of the thermogram shows that a sudden change in the light intensity occurs concomitantly with the evolution of the CO_2 peak at about 470°C. The light intensity I_0, after the 470°C peak has evolved, corresponds to that of a blank filter. This demonstrates that the light-absorbing species in the sample are combustible and carbonaceous — the graphitic carbon referred to above. The carbonate peak evolves at about 600°C; and as carbonate is not light absorbing, it does not change the optical density of the sample. In addition to black carbon and carbonate, the thermogram in Figure 2 also shows several distinct groups of peaks at temperatures below $\sim$ 400°C that correspond to various organics.

The potential for applications of EGA to the characterization of nitrogeneous species is illustrated in Figure 3, where NO_x thermograms of NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, and $NaNO_3$ are shown. It is obvious from the figure that distinguishing the principal nitrogen species is feasible by this technique.

The ESCA used in these experiments is a modified AEI ES–200 electron spectrometer which has been updated by the installation of a Surface Science Laboratories Model 239G position-sensitive photoelectron detector. The modifications also included replacement of all lens and analyzer power supplies, as well as changing to a modern microprocessor-based data system. Data collection with the modified spectrometer is approximately 10 times as rapid as with the original, thus substantially decreasing sample degradation during analysis.

Results and Discussion

The analytical results of our previous ESCA work (3) can be summarized as follows:

Sulfur is found to be predominantly in a +6 oxidation state, i.e., sulfate. Other chemical states of sulfur have also been

observed, although these seldom approach sulfate concentrations. Generally, at high pollutant concentrations sulfate is practically the only sulfur species present. Nitrogen can be present in an oxidized and a reduced form. The oxidized form has been identified as nitrate, while the reduced form consists of ammonium and a group of species consisting of particulate amines and amides, N_x. These N_x species were first discovered by ESCA (6) and are easily distinguished from ammonium by a $\sim$ 2 eV chemical shift of the N(1s) peak.

Attempts were made to prove the existence of the particulate amines by other techniques with only limited success. At best indirect evidence (7) was obtained from the fact that nitrate and ammonium cannot account for total particulate nitrogen as determined by combustion. However, the observed nitrogen deficiency was much less than indicated by ESCA. At attempt to detect N_x by infrared spectroscopy (8) failed because of interfering absorption bands.

In order to detect N_x species by EGA, we used the results of our earlier ESCA analyses (6), which demonstrated that exposing a sample to vacuum and x-ray bombardment or heat results in the volatilization of most of the nitrate and ammonium salts. Thus, in a sample exposed to vacuum, the only major nitrogeneous species will be N_x. This is illustrated in Figures 4a and b. The NO_x thermograms of the original and vacuum-exposed samples are shown in Figures 4c and d. The ESCA spectra show that the principal species are volatile nitrate and ammonium, probably present as ammonium nitrate and ammonium sulfate and nonvolatile N_x. The corresponding thermograms show a reduction in intensity in the triplet located between 150-300°C, assigned to ammonium nitrate and ammonium sulfate. Peaks at $\sim$ 350 and 450°C and the peak at $\sim$ 550°C are unchanged, however. The first two probably correspond to N_x, while the last peak is most likely due to a metal nitrate.

We have used the ESCA results to provide empirical information about the apparent stoichiometry of sulfate, ammonium, and nitrate ions and other elements and species. Wet chemical analyses performed at several laboratories seemed to contradict some of the conclusions reached from ESCA studies. For example, total reduced nitrogen as determined by ESCA often agrees with the determination of ammonium by wet chemical methods. A consequence of this discrepancy is that in analyses where wet analysis would indicate ammonium sulfate, ESCA would suggest ammonium bisulfate, based on the assumption that particulate N_x species are not associated with sulfate. This assumption may not be valid, because it has been demonstrated (1) that a large fraction of N_x present in the original sample may be hydrolyzed to ammonium and removed by water extraction.

An insight into this apparent inconsistency may be achieved by combined ESCA and EGA analysis. Figure 5 shows the ESCA spectrum of the N(1s) region of a sample collected in Gaithersburg,

Maryland. In addition to a small nitrate peak, a pronounced ammonium peak is also seen. This sample contains a very small concentration of N_x that is evidenced only by a slight asymmetry of the ammonium peak. This sample contains enough ammonium to almost completely neutralize the sulfate as determined by ESCA. The conclusion is that here the sulfate is in the form of ammonium sulfate. The NO_x thermogram of the same sample is shown in Figure 6. The positions of NH_4NO_3 and $(NH_4)_2SO_4$ thermogram peaks are indicated in the figure. This thermogram suggests that the principal counterion for sulfate is ammonium, not N_x, and that the sulfate is present as $(NH_4)_2SO_4$. This is consistent with the ESCA observations.

This situation is quite different for an Anaheim sample whose N(1s) ESCA spectrum is shown in Figure 7. Here in addition to NO_3^- and NH_4^+, the N_x peak is clearly seen. Volatility in ESCA vacuum indicates that the nitrate in this sample is present as NH_4NO_3, and therefore a significant portion of the ammonium is associated with the nitrate. The remainder of the ammonium is insufficient to provide counterions for the sulfate. This ESCA result suggests an ammonium-deficient sulfate compound such as ammonium bisulfate. We note that if the entire reduced nitrogen were hydrolyzed, there would be sufficient ammonium to conclude that the sulfate is present as ammonium sulfate.

The thermogram of this sample is shown in Figure 8. The ammonium nitrate peak and the first peak of ammonium sulfate match closely the positions of standard compounds. However, the peak at 270°C is noticeably shifted from the second ammonium sulfate peak, although the overall appearance of the doublet is similar to that of ammonium sulfate. A tentative explanation of this observation is that the sample does not contain pure ammonium sulfate, but rather that some of the ammonium ions are replaced by a charged organic nitrogen complex. This complex should produce the right chemical shift (relative to ammonium) in the ESCA spectrum, decompose at a lower temperature than ammonium bisulfate, and hydrolyze to ammonium in water solution.

Acknowledgments

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K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S.E.; Lindgren, I.; and Lindberg, B.J. <u>Nova Acta Regiae Soc. Sci. Ups., Ser. IV</u> 1967, 20.

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5. Dod, R.L.; Rosen, H.; and Novakov, T. <u>in</u> "Atmospheric Aerosol Research Annual Report 1978-78"; Lawrence Berkeley Laboratory Report LBL-8646, 1980; p. 2.

6. Chang, S.G.; and Novakov, T. <u>Atmos. Environ.</u> 1975, <u>9</u>, 495.

7. Spicer, C.W. <u>Atmos. Environ.</u> 1977, <u>11</u>, 1089.

8. Chang, S.G.; and Novakov, T. <u>in</u> "Atmospheric Aerosol Research Annual Report 1976-77"; Lawrence Berkeley Laboratory Report LBL-6819, 1977; p. 57.

Figure Captions

Figure 1. Schematic diagram of thermal analysis (EGA) apparatus.

Figure 2. Carbon and optical thermogram of a Berkeley, California, ambient particulate sample.

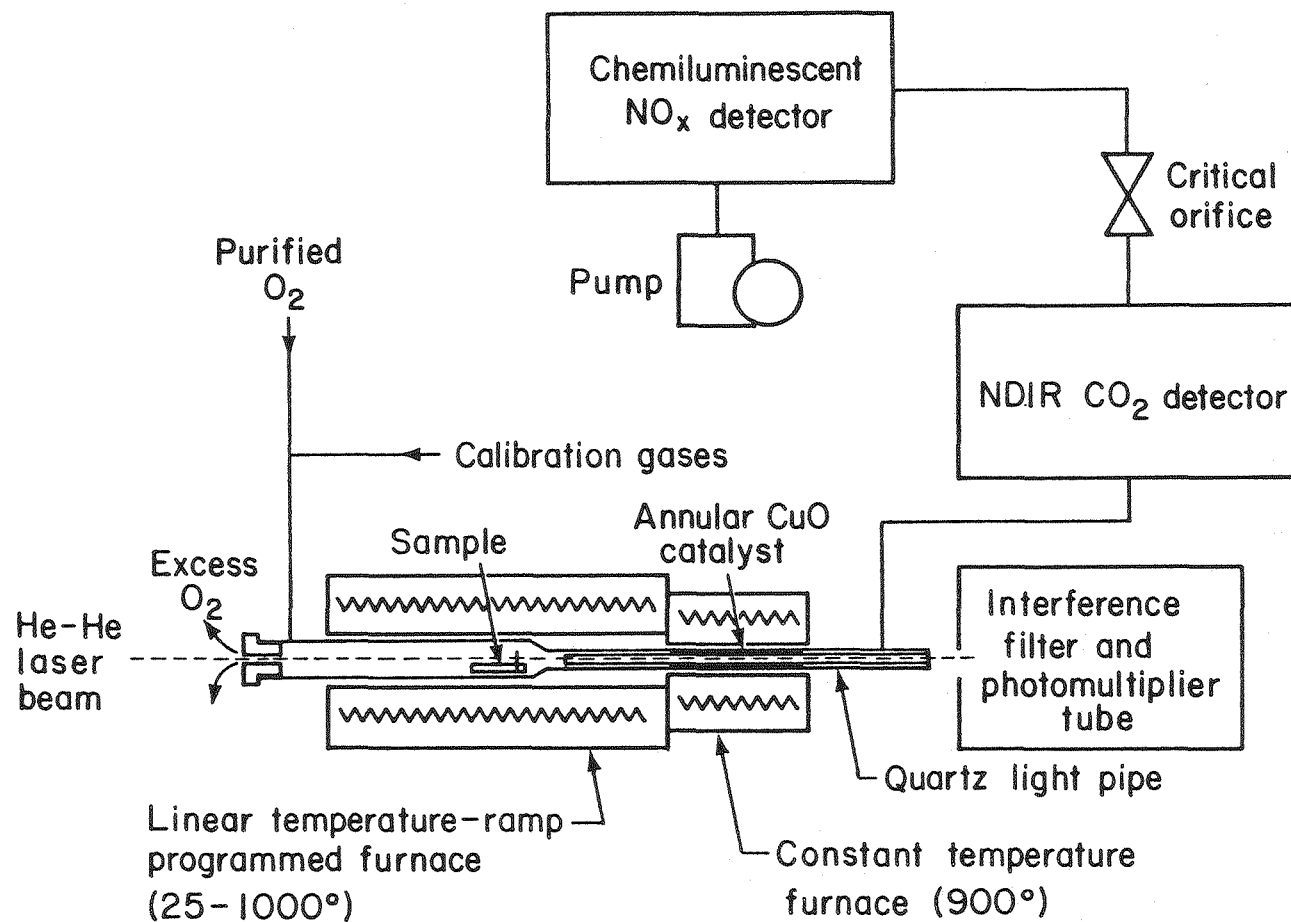Figure 3. NO_x EGA thermograms of nitrogen standard compounds.

Figure 4. ESCA spectra and NO_x thermograms from an ambient particulate sample from Riverside, California; before and after exposure to vacuum.

Figure 5. N(1s) ESCA spectrum of 24 April 1979 ambient particulate sample from Gaithersburg, Maryland.

Figure 6. NO_x thermogram of 24 April 1979 ambient particulate sample from Gaithersburg, Maryland.

Figure 7. N(1s) ESCA spectrum of 27 July 1979 ambient particulate sample from Anaheim, California

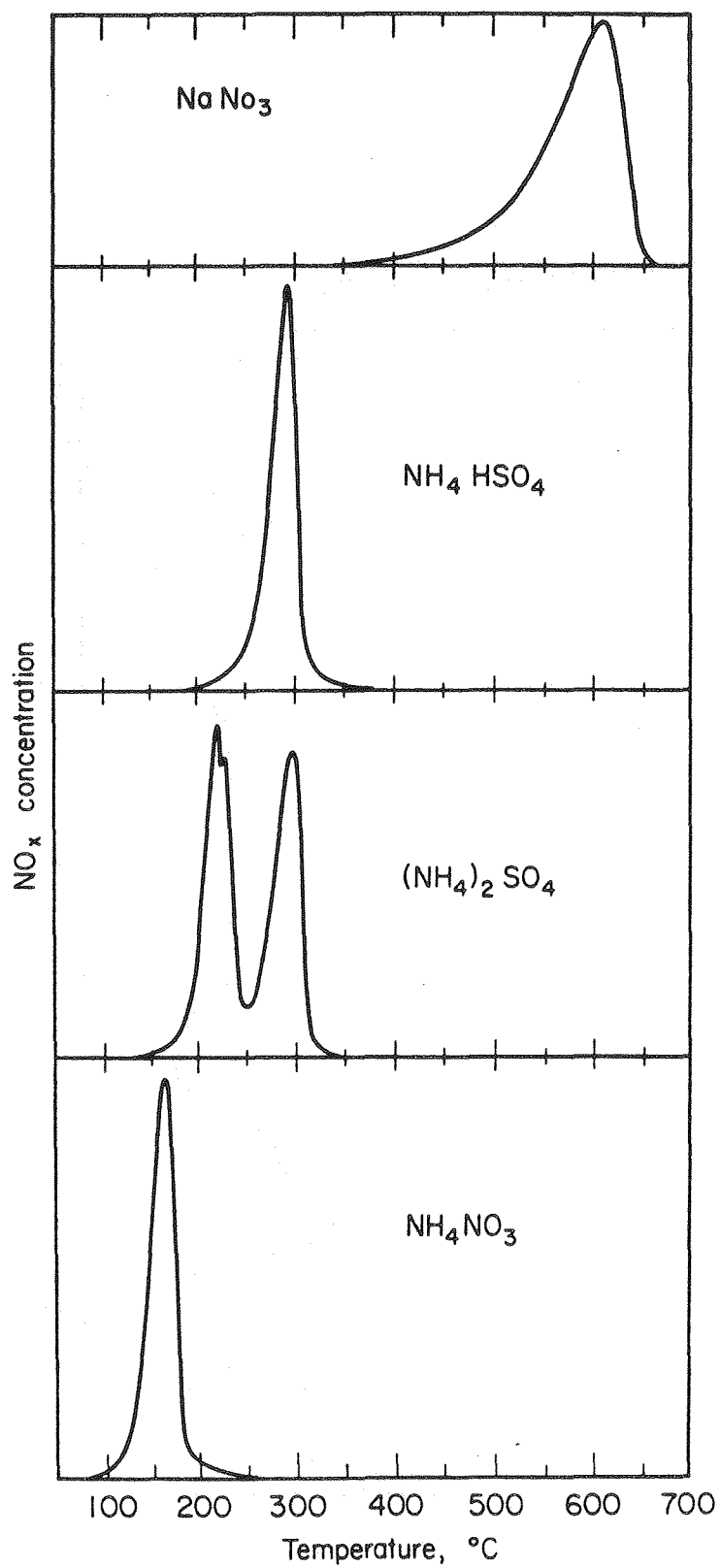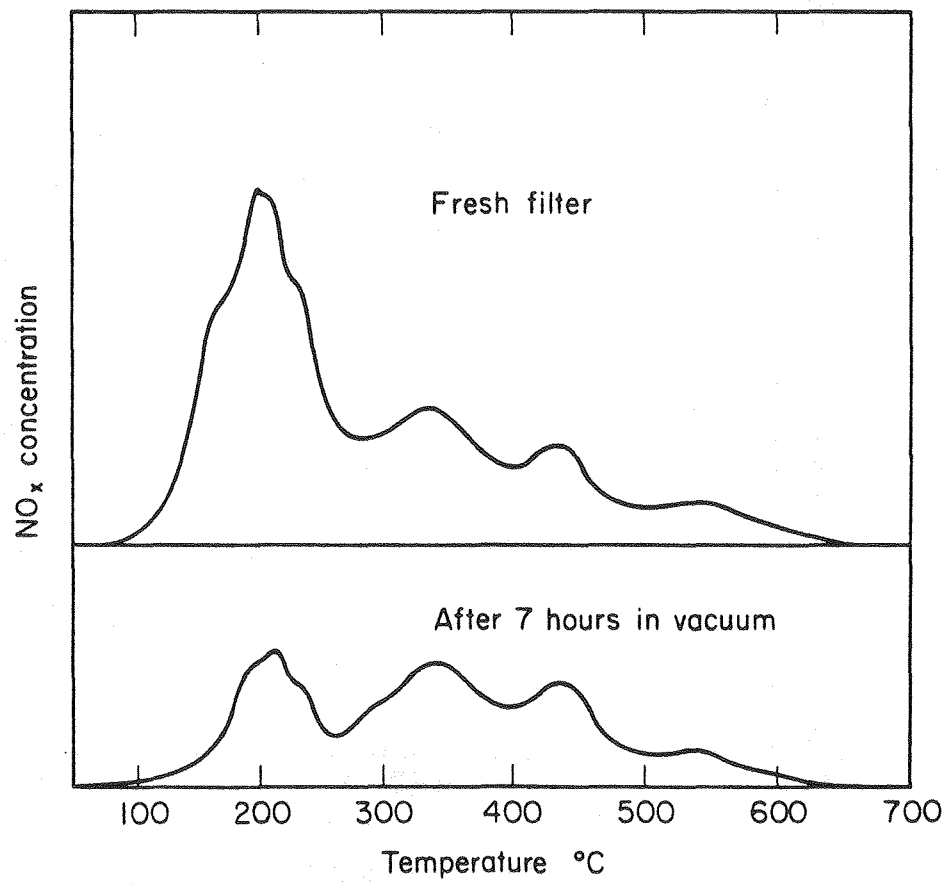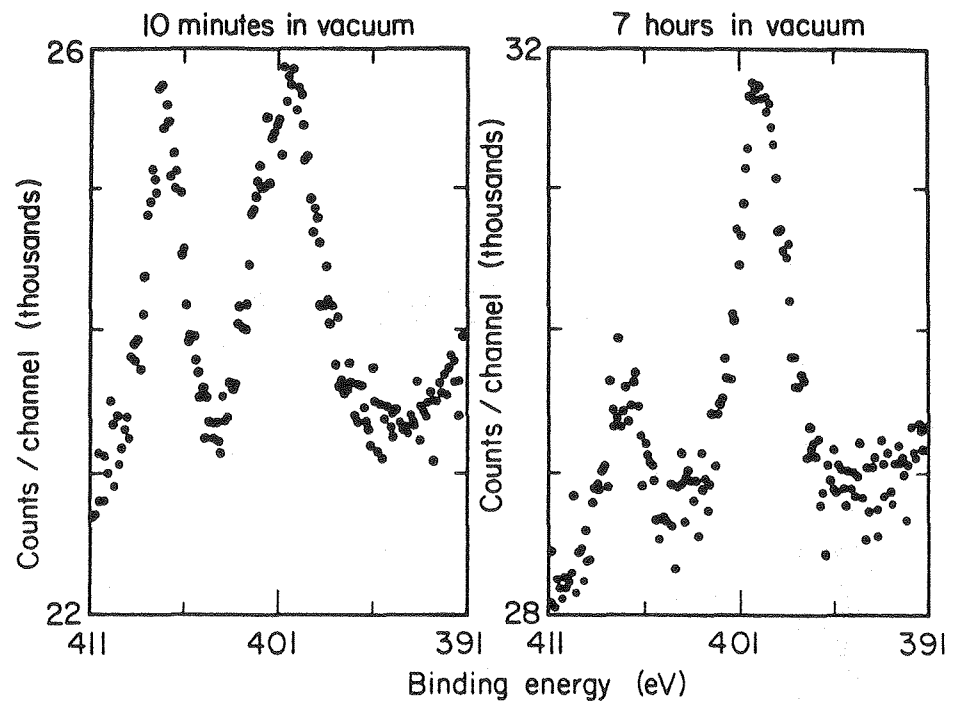Figure 8. NO_x thermogram of 27 July 1979 ambient particulate sample from Anaheim, California.

Chemiluminescent NO$_x$ detector

Pump

Critical orifice

NDIR CO$_2$ detector

Purified O$_2$

Calibration gases

Annular CuO catalyst

Sample

Excess O$_2$

He-He laser beam

Interference filter and photomultiplier tube

Quartz light pipe

Linear temperature-ramp programmed furnace (25-1000°)

Constant temperature furnace (900°)

XBL8III-1623

Figure 1

XBL 807-1696

Figure 2

Figure 3

Figure 4

NITROGEN 1 S

Figure 5

XBL 8III-1622

Figure 6

NITROGEN 1 S

Figure 7

Figure 8